

Reaction of Dissolved Zinc with Fuel Crud in Simulated PWR Coolant at 328 °C

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1. Introduction

The first purpose of zinc addition to PWR primary coolant was to reduce the radiation field and subsequent personnel exposure. The beneficial effect of zinc addition in the reduction of radiation field is basically attributed to a decrease of corrosion rates and corrosion product release rates from primary system materials in PWRs [1,2], resulting in radioactive source term reduction. The beneficial effect of zinc was also reported in mitigating stress corrosion cracking of stainless steels and Ni-based alloys in simulated PWR primary water chemistry [3]. Zinc divalent cations have been known to replace Ni, Fe, Co, or radioactive Co cations in spinel oxides formed on nickel-based alloys and stainless steels under PWR primary water conditions [4,5].

A lot of research on zinc addition has been performed from the view point of corrosion rate, corrosion release rate, and zinc incorporation in oxide films of nickel-based alloys and stainless steels in laboratories and operating PWRs. However, open literature about the effects of zinc injection on fuel crud is scarce, possibly because of experimental difficulty in laboratories and extremely high-level radiation from burned fuel assemblies.

Despite its benefits, there are still concerns limiting zinc addition initiative, especially in high duty cores. The major concerns are related with the potential impacts on fuel integrity. First of all, added zinc could induce the buildup of corrosion products on fuel cladding surfaces. The zinc in the coolant could be incorporated into the fuel crud and substitute cations as in oxide films of nickel-based alloys and stainless steels. The zinc could also affect the corrosion rate of fuel claddings. In this study, therefore, zinc incorporation behavior into newly forming fuel crud and pre-existing fuel crud was investigated under simulated PWR primary coolant conditions using a fuel crud deposition system.

2. Experimental

2.1 Material and Solutions

Zirconium-based fuel cladding tubes were used for fuel crud deposition and zinc incorporation tests. The test solution used in this work was composed of 2 ppm Li as LiOH and 1000 ppm B as H₃BO₃ in deionized water to simulate the primary coolant of PWRs. If necessary, depleted zinc acetate-dehydrate was added to this solution. Crud source solution for deposition tests

was made up by adding Ni- and Fe-ethylenediaminetetraacetic acid to the primary coolant containing 2.0 ppm Li and 1000 ppm B.

2.2 Zinc Incorporation Test into Newly Forming Crud

Zinc incorporation behavior during crud formation on fresh cladding tubes was investigated using the KAERI fuel crud deposition loop system. The detailed information for the system is given elsewhere [6].

Dissolved oxygen (DO) content in solutions was controlled below 5 ppb by continuously blowing hydrogen gas into all the solution tanks. Dissolved hydrogen content (DH) was maintained at 35 cm³/kg H₂O (STP) by controlling the hydrogen overpressure of the solution tanks. The simulated primary coolant circulated with a flow rate of 280 ml/min via a high pressure pump. The temperature of the flowing coolant through the annular space surrounding the tube specimen in the autoclave was maintained at 328 °C. A heat flux of 65 W/cm² was supplied to the tube surface by a cartridge heater. When all these parameters reached target conditions, the injection of the crud source solution started to the downstream of the preheater with a flow rate of 1.0 mL/min. Therefore, the injecting crud source solution was mixed in the primary coolant stream, which finally gave a concentration of 0.50 ppm Fe and 0.28 ppm Ni without zinc (Case #1) and with 20 ppb zinc (Case #2) in the autoclave.

2.3 Zinc Incorporation Test into Pre-existing Crud

Zinc incorporation behavior into pre-existing crud was investigated using cladding tubes with pre-formed thick crud. To prepare pre-existing crud before adding zinc, crud deposition was first performed in the simulated primary coolant containing 2.0 ppm Li and 1000 ppm B without zinc using the KAERI deposition loop system. In this test, the concentration of crud source solution containing nickel and iron increased to form a thick crud layer. The injected source solution was mixed and diluted in the flowing primary coolant, resulting in a concentration of 8 ppm Fe and 6 ppm Ni in the test section. After deposition of 240 h at 328 °C, the loop system was shut down and the cladding tube covered with crud was removed from the autoclave to analyze the crud (Case 3#). In Case #4, after deposition of 240 h, the loop system was shut down and cleaned by circulating the primary coolant containing 2.0 ppm Li and 1000 ppm B to remove the residual crud source in the loop. And then, the loop system was restarted and the deposited cladding tube was exposed to the

circulating primary coolant containing 2.0 ppm Li and 1000 ppm B with 60 ppb zinc for 500 h at 328 °C without crud source injection.

3. Results and Discussion

3.1 Zinc Incorporation Behavior into Newly Forming Crud

Regardless of zinc addition, crud particles of polyhedral shape were uniformly formed on the cladding tube surfaces. The particles showed clear crystalline facets and ranged up to several microns in size.

Crud particles were vertically machined to make TEM specimens using the FIB milling technique and analyzed using STEM-EDS. Fig. 1 shows a STEM image and EDS elemental composition maps of crud particles formed under the no zinc condition (Case #1). Fe, Ni and O were detected. Therefore, the elemental mapping indicates that the polyhedral-shaped particles are oxides consisting of Fe and Ni. Based on the STEM-EDS analyses of the crud particles, the crud was identified as nickel ferrites with an average spinel stoichiometry of $Ni_{0.26}Fe_{2.74}O_4$. On the other hand, zirconium oxide layer with about 1~2 μm thickness was observed, which were formed through internal oxidation of the zirconium based cladding tube during the test.

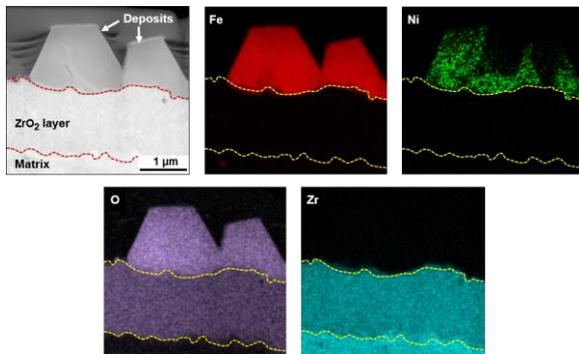


Fig. 1. STEM image and EDS elemental mapping of fuel crud formed under the no zinc condition (Case #1).

Fig. 2 gives a STEM image and elemental maps of crud particles formed under the 20 ppb zinc condition (Case #2). As seen in the maps, zinc was found in the particles and zinc content incorporated in the crud ranged up to 2.6 at. %. The quantitative STEM-EDS results revealed that the crud was nickel ferrites containing zinc with an average spinel formula of $Ni_{0.23}Zn_{0.14}Fe_{2.63}O_4$. On the other hand, zinc was not found in zirconium oxide layer, indicating that zinc did not react with zirconium oxide.

3.2 Zinc Incorporation Behavior into Pre-existing Crud

Fig. 3 shows SEM micrographs on the surfaces and cross-sections of thick fuel crud formed under the no zinc condition of Case #3 and after the subsequent

exposure to the 60 ppb zinc coolant under the condition of Case #4. From the top down view of the deposited surfaces, it is observed that the crud layer has numerous micro-pores and uneven thickness over the cladding surfaces. A distinct morphological change was not found after the pre-formed crud was exposed to the 60 ppb zinc coolant for 500 h. Micro-pores were clearly observed on the cross-sections of the crud, which were milled using the FIB.

The 2D porosity of the crud was measured using an image analyzer and the average porosity was 37% for Case #3 and 39% for Case #4. Therefore, it is concluded that the morphology and porosity of the fuel crud were not affected by the subsequent exposure to the zinc containing coolant.

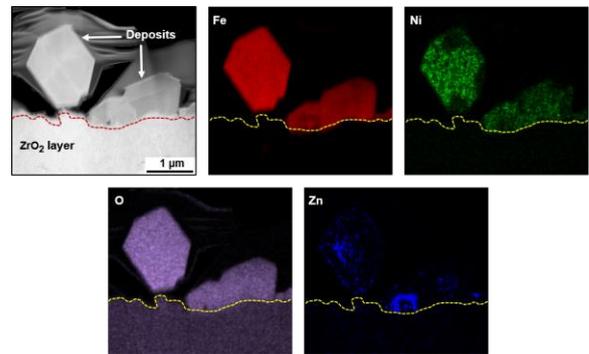


Fig. 2. STEM image and EDS elemental mapping of fuel crud formed under the no zinc condition (Case #2).

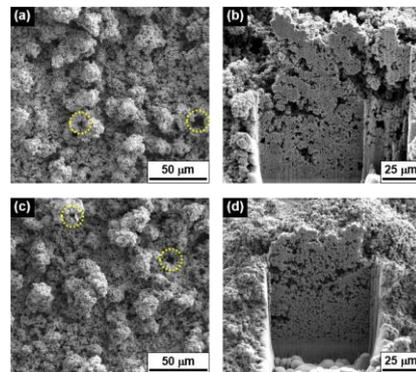


Fig. 3. SEM micrographs of fuel crud formed (a, b) under the condition of Case #3 and (c, d) after the subsequent exposure to the 60 ppb zinc coolant under the condition of Case #4. The dotted circles in (a) and (c) show examples of large micro-pores. (b) and (d) are the cross-sections of the crud milled using the FIB technique.

Fig. 4 presents a STEM image and EDS elemental maps of fuel crud particles formed under the condition of Case #3 without zinc. The EDS maps indicated that the crud was composed of Fe, Ni, and O. However, surprisingly, no zinc was detected in the crud of Case #4 as shown in Fig. 5, although the pre-formed crud were exposed to the 60 ppb zinc coolant for 500 h. This result was not changed even after repeating the experiment once more, indicating that no zinc was incorporated in the crud during the exposure to the zinc coolant.

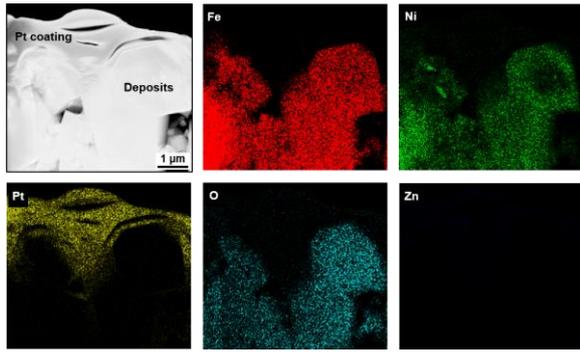


Fig. 4. STEM image and EDS elemental mapping of fuel crud formed under the no zinc condition (Case #3).

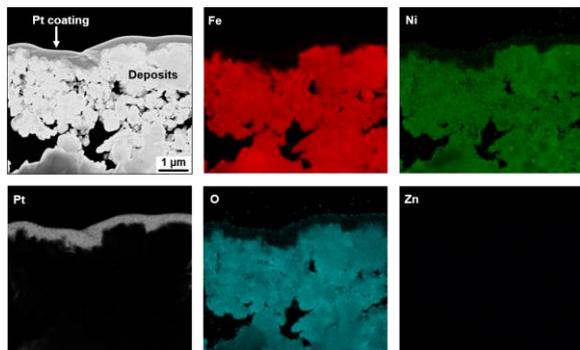


Fig. 5. STEM image and EDS elemental mapping of the fuel crud after the pre-formed crud was exposed to the 60 ppb zinc coolant under the condition of Case #4.

4. Discussion and Summary

The dissolved zinc divalent cations have been reported to substitute cations such as Ni^{2+} , Co^{2+} , and Fe^{2+} in newly forming spinel oxides on the fresh surfaces and in the pre-grown oxides of nickel-based alloys and stainless steels in PWR primary coolant conditions [4,5]. The substitution of zinc cations in the oxides can be attributed to their higher site preference energy at tetrahedral sites, compared with those of other cations [7,8]. Zinc incorporation in fuel crud has also been reported in operating PWRs with zinc water chemistry [9,10]. However, in these cases, it was difficult to determine whether zinc was incorporated in newly forming crud after zinc addition, or in pre-existing crud before zinc addition, or in both. From Fig. 2, it is now clearly demonstrated that zinc divalent cations dissolved in the primary coolant are incorporated in newly forming fuel crud. This indicates that zinc ions involve in the nucleation and growth process of the crud, competing with other cations to occupy the lattice sites. At this time, due to the incorporation of zinc cations in the newly forming crud, surplus nickel and radiocobalts (^{58}Co , ^{60}Co) defeated by zinc remain in the flowing coolant and thus can be removed from the coolant through ion exchange membranes and filters in the system, thereby contributing to a reduction of radiation fields.

However, zinc substitution was not observed in the pre-existing crud even after exposure to the coolant containing 60 ppb zinc up to 500 h. But that does not mean that zinc substitution into the pre-formed crud is thermodynamically impossible. The free energy of formation of zinc-containing spinels is higher than that for zinc replacement of divalent cations such as Co, Fe and Ni [1]. That is, the formation of zinc-incorporated spinel is thermodynamically more favored. Therefore, it is thought that the rate of zinc substitution into the pre-formed crud is very slow.

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